Thermodynamics: Classical to Statistical

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Lecture - 32

Problems on Statistical Thermodynamics - 4

Problems

Problem 1:

Show that the vibrational entropy of a 3d-solid, described by the Einstein model, is

$$S = 3Nk_B\left[\frac{x}{e^x - 1} - \ln(1 - e^x)\right]$$

where $x = h\nu / k_B T$.

Solution:

We know, entropy, $S = k_B \ln Q + \frac{<E>}{T}$ and average energy, $<E> = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$.

Now the total partition function is $Q = q_{vib}{}^{3N} = \left[\frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}\right]^{3N}$. Now,

$$\ln Q = -3N\beta h\nu / 2 - 3N\ln(1 - e^{-\beta h\nu})$$

$$\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = -\frac{3Nh\nu}{2} - \frac{3N}{1 - e^{-\beta h\nu}}(-e^{-\beta h\nu})(-h\nu)$$

$$<E> = \frac{3Nh\nu}{2} + \frac{3Nh\nu}{e^{\beta h\nu} - 1}$$

Substituting all the above values, we get

$$S = k_B\left[-\frac{3N\beta h\nu}{2} - 3N\ln(1 - e^{-\beta h\nu})\right] + \frac{1}{T}\left[\frac{3Nh\nu}{2} + \frac{3Nh\nu}{e^{\beta h\nu} - 1}\right]$$

$$S = 3Nk_B\left[\frac{x}{e^x - 1} - \ln(1 - e^x)\right]$$

Using $\beta = 1/k_B T$ and $x = h\nu / k_B T$.

Problem 2:

Consider a solid, where a fixed number of atoms, 'N' form into a crystal, where the atoms sit in an ordered array on the sites of a lattice. An Schottky defect is a lattice site without an atom. Assume that there are 'n' number of lattice sites that do not have any atom and each defect costs energy of epsilon. Calculate the Helmholtz free energy as a function of 'n'. Also show that the equilibrium number of defects can we written as

$$< n >= \frac{N}{e^{\beta\varepsilon} - 1}$$

Solution:

It is clear that 'N' number of sites in the lattice are occupied and 'n' number of sites in the lattice are unoccupied.

So, total number of lattice site is N plus n.

The weight of the distribution, $w = \frac{(N+n)!}{N!n!}$

$$\ln w = \ln(N+n)! - \ln N! - \ln n!$$

Using Sterling's approximation, $\ln w = (N+n)\ln(N+n) - N\ln N - n\ln n$

So, entropy, $S = k_B \ln w$

$$S = k_B[(N+n)\ln(N+n) - N\ln N - n\ln n]$$

$$A(n) = < E > -TS \quad \text{and} \quad < E >= n\varepsilon$$

$$A(n) = n\varepsilon - k_B[(N+n)\ln(N+n) - N\ln N - n\ln n]$$

The minimization of A (n) with respect to n gives the equilibrium number of defects.

$$\frac{dA(n)}{dn} = \varepsilon - k_B T \ln\frac{N+n}{n} = 0$$

$$n = \frac{N}{e^{\beta\varepsilon} - 1}$$

where $\beta = 1/k_B T$.

Problem 3:

A two level system of N ($N=n_1+n_2$) number particles is distributed between two states 1 and 2 with energies E_1 and E_2 respectively. The system is in contact with a reservoir at temperature T K. If a single quantum emission occurs, population changes from n_2 to n_2-1 and n_1 to n_1+1.

For $n_1 >> 1$ and $n_2 >>1$, obtain (a) the entropy change of the system, (b) the entropy change of the reservoir and (c) from a and b, derive the Boltzmann relation.

Solution:

Before emission,

The number of particles in energy state $E_1 = n_1$

The number of particles in energy state $E_2 = n_2$

The weight of the distribution, $w_1 = \frac{N!}{n_1!n_2!} = \frac{(n_1+n_2)!}{n_1!n_2!}$

The entropy, $S = k_B \ln w_1 = k_B \left[n_1 \ln \frac{n_1+n_2}{n_1} + n_2 \ln \frac{n_1+n_2}{n_2} \right]$

After emission,

the number of particles in energy state $E_1 = n_1+1$

the number of particles in energy state $E_2 = n_2-1$

The weight of the distribution, $w_2 = \frac{N!}{(n_1+1)!(n_2-1)!} = \frac{(n_1+n_2)!}{(n_1+1)!(n_2-1)!}$

The entropy, $S = k_B \ln w_2 = k_B \left[(n_1+n_2)\ln(n_1+n_2) - (n_1+1)\ln(n_1+1) - (n_2-1)\ln(n_2-1) \right]$

(a) The change in entropy of the system due to this process,

$$\Delta S_1 = S_2 - S_1 = k_B \ln \frac{n_2}{n_1+1}$$

$$\Delta S_1 \approx k_B \ln \frac{n_2}{n_1} \quad \text{as} \quad n_1 >>1$$

(b) Entropy change of the reservoir, $\Delta S_2 = \frac{E_2 - E_1}{T}$.

(c) Now,

$$\Delta S_1 = -\Delta S_2$$

$$k_B \ln \frac{n_2}{n_1} = \frac{E_2 - E_1}{T}$$

$$\frac{n_2}{n_1} = e^{-\frac{E_2-E_1}{k_B T}} = e^{-\beta(E_2-E_1)}$$

So, this is nothing but the Boltzmann relation.

Problem 4:

The third law of thermodynamics asserts that $\lim_{T\to 0} S = 0$ for any macroscopic system. What condition has to be satisfied for this claim to hold?

Solution:

We know, partition function, Q, is

$$Q = \sum_i \Omega_i e^{-\beta E_i} = \Omega_0 e^{-\beta E_0} + \Omega_1 e^{-\beta E_1} + \Omega_2 e^{-\beta E_2} + \ldots$$

where Ω_0, Ω_1, Ω_2 etc, are the degeneracies of the ground state, first excited state and second excited state, etc, and, E_0 is the ground state energy; E_1 is the first excited state energy, E_2 is the second state energy.

$$Q = \Omega_0 e^{-\beta E_0}\left[1 + \frac{\Omega_1}{\Omega_0} e^{-\beta \Delta E_1} + \frac{\Omega_2}{\Omega_0} e^{-\beta \Delta E_2} + \ldots.\right]$$

where, $\Delta E_1 = E_1 - E_0$ and $\Delta E_2 = E_2 - E_0$ and so on.

Now, at low temperature ($T \to 0$ or $\beta \to \infty$), $\beta \Delta E_1 >> 1$ and so on.

$$Q = \Omega_0 e^{-\beta E_0}$$

$$\ln Q = \ln \Omega_0 - \beta E_0$$

$$k_B \ln Q = k_B \ln \Omega_0 - \beta E_0$$

$$k_B \ln Q = k_B \ln \Omega_0 - E_0 / T$$

$$S = k_B \ln \Omega_0$$

So, this says $S \to 0$, when $\Omega_0 \to 1$.

So, it says that ground state must be non-degenerate or, the degeneracy of the ground state must be 1, in order to hold the relation, $\lim_{T \to 0} S = 0$